Permeability of oxygen through membranes of poly(cyclohexyl acrylate)

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The permeability of oxygen through membranes of poly(cyclohexyl acrylate) at temperatures in the vicinity of the glass transition temperature (T_g) is determined using an electrochemical experiment. The diffusion coefficient of the gas follows Arrhenius behaviour with an activation energy of 22 kcal mol^{-1}, a surprisingly high value if it is considered that the range of activation energies observed in most systems is 1–20 kcal mol^{-1}. The interpretation of the free volume of the membrane at T_g suggests that the critical volume necessary for permeation of the gas to take place is nearly four times lower than the value of this parameter for the mechanical and dielectric processes. It is suggested that bulky side groups may aid the transport of gas in the glassy state but presumably hinder it in the rubbery state.

(Keywords: poly(cyclohexyl acrylate); membrane; permeability; oxygen)

INTRODUCTION

The diffusion of small molecules through membranes is a subject of great interest with important practical implications[1]. Though the mechanisms involved in diffusional transport are poorly understood, it is evident that chain dynamics plays an important role in the process[2,3]. In fact, a detailed molecular diffusion model could be developed provided that the frequency amplitude and average separation of polymer chains are known because, in this case, the exact nature of the interactions between the penetrant and the entangled chains could be established.

The dependence of the diffusion of penetrant on chain dynamics becomes clear if we consider that below the glass transition temperature (T_g), where the chains are frozen and only short-range motions are permitted, the value of the diffusion coefficient is severely reduced with respect to that of the diffusion coefficient above T_g. Structural factors have a significant effect on the diffusional process[4–9]. Studies performed on methyl-substituted phenyldiamines reveal that the rigidity and non-planar structure of the polymer chains, in conjunction with the bulkiness of methyl groups, make chain packing inefficient, resulting in an increase of both diffusion and solubility coefficients of gases[9]. The influence of chain packing has also been shown in diffusional studies performed on oriented semicrystalline films[10]. Obviously, the microstructure of the membrane also plays an important role in the diffusional processes. Thus recent studies[11] carried out on compression-moulded films prepared from the liquid-crystalline copolyester of hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) suggest that the more hindered mobility of the naphthyl unit restricts penetrant mobility, on the one hand, and that transport may likely occur in a small volume fraction of less dense boundary phase, on the other hand. All the evidence at hand seems to indicate that the diffusional process is conditioned by the free volume, and therefore sorption and diffusion take place almost exclusively through the amorphous regions.

The purpose of this work is to describe a rapid method of measuring the permeability of oxygen through membranes, by using the membrane-covered electrode technique. Another goal is to relate the critical volume necessary for the diffusional process to occur with the critical volume necessary for both mechanical and dielectric relaxation processes to take place. Thus value of the diffusion coefficient of oxygen through membranes of poly(cyclohexyl acrylate) (PCA) in the vicinity of T_g are reported. The results are discussed in terms of the free volume at T_g (refs. 12, 13), by using for this quantity the results obtained from the critical interpretation of the mechanical and dielectric relaxation times associated with the glass–rubber processes in PCA[14].

EXPERIMENTAL

Cyclohexyl acrylate was synthesized at 0°C by the addition of 0.30 mol of freshyl distilled acryloyl chloride to an aqueous medium containing 0.25 mol of cyclohexanol, 20% dioxane and 5% NaOH. The monomer was

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extracted twice with ether, washed with distilled water, dried overnight with calcium chloride and then with calcium hydride, and finally distilled at reduced pressure.

Poly(cyclohexyl acrylate) (PCA) was obtained at 50°C by radical polymerization of cyclohexyl acrylate in benzene solution using azobisisobutyronitrile (AIBN) as initiator. The polymer was precipitated with methanol, filtered and dried under vacuum. The number-average molecular weight of the polymer, measured with a Knauer high-speed membrane osmometer, was found to be 150 000. The glass transition temperature determined by dilatometry has a value of 25°C.

A membrane of poly(cyclohexyl acrylate), 0.275 mm thick, was prepared by casting from a solution of the polymer in chloroform. The membrane was dried under high vacuum for several days prior to its use in the diffusion measurements. An experimental assembly with small modifications with respect to that frequently utilized in the determination of oxygen permeability through contact lenses[15–18] was used. Here the membrane is not in direct contact with the sensor as occurs in hydrogels, but through a solution. In brief, it consists of a permeometer model 201T (Rheder Development Co.) in which the polarographic cell is a solid cylindrical cathode of 24 carat gold (4.25 mm diameter and 6 mm long). The anode is a hollow cylinder made of silver (purity 99.9%), 7 mm long, the inner and outer diameters being 5 and 10 mm, respectively. A thermistor is installed into the anode to monitor the temperature of the cell and the membrane during the measurements. The temperature was controlled by a thermostat of water, which was adjusted in such a way that changes in this parameter higher than 0.1°C were not permitted. Details of the experimental assembly are given in *Figure 1*

THEORY

The oxygen flux through a membrane can be determined from the measurement of the electric current in a potentiostatic cell. The reduction in the cathode is:

$$O_2+2H_2O+4e^-\rightarrow 4OH^-$$

The oxygen flux density across a membrane of thickness L is assumed to obey Fick's law:

$$J=-D\,\partial C/\partial x \tag{1}$$

where D is the diffusion coefficient, which is considered to be constant in the membrane–solution system, C is the oxygen concentration in the solution and x is the normal distance to the surface of the membrane. The transport process is usually described by introducing into equation (1), instead of the concentration, the partial pressure p of the oxygen in the air, which is in equilibrium with the concentration of this gas in the liquid phase. Both magnitudes are related by Henry's law:

$$C=kp \tag{2}$$

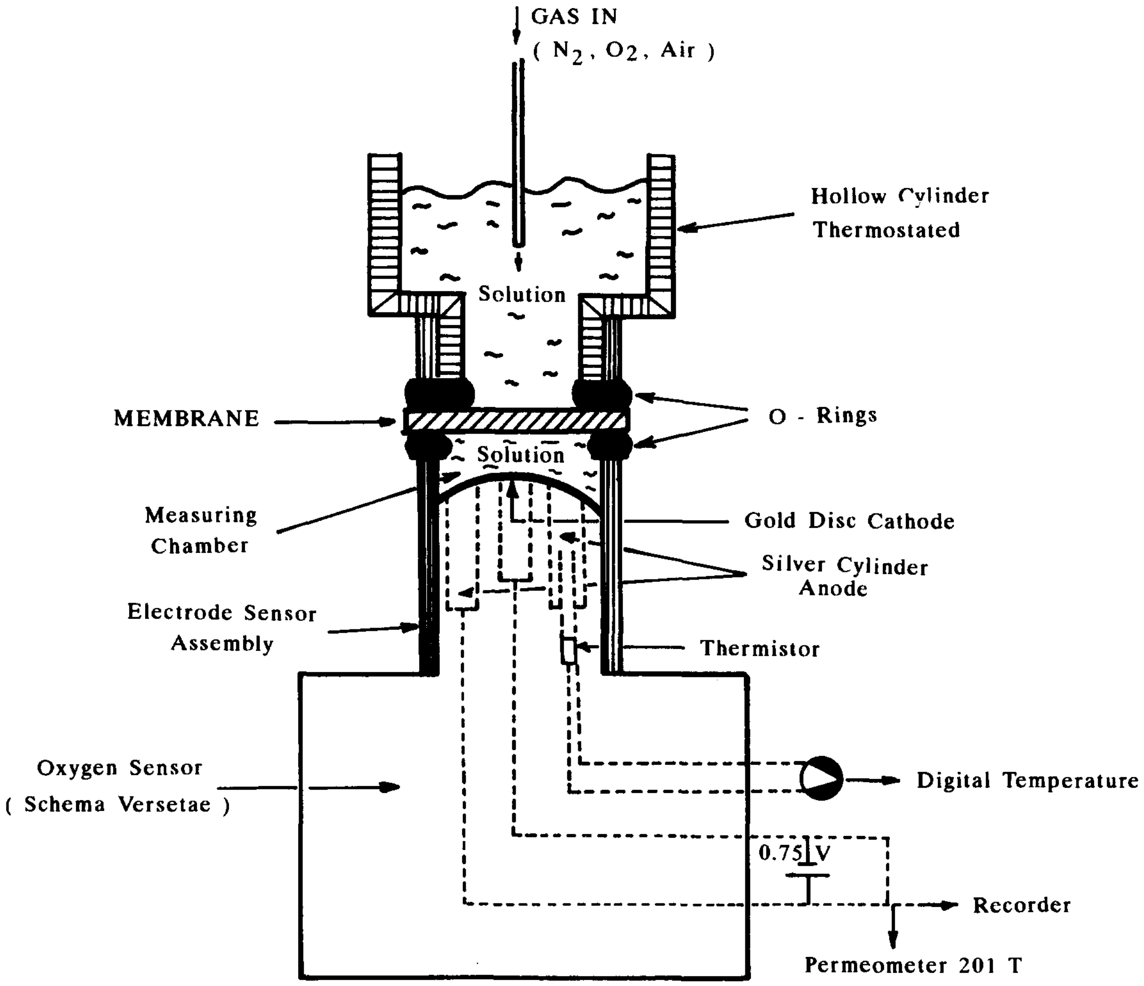

Figure Details of the experimental assembly

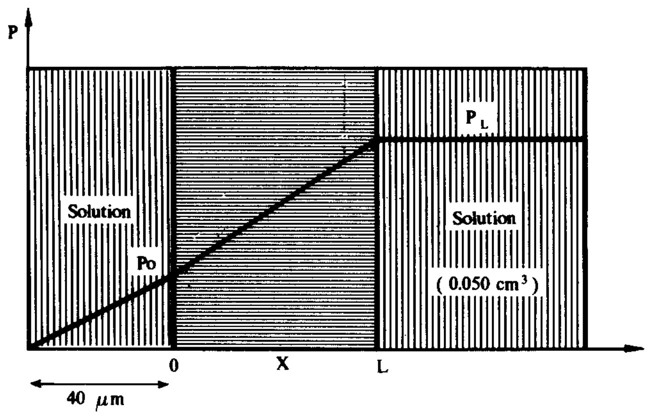

Figure 2 Oxygen pressure profile across the membrane and the solutions surrounding it

where k is the solubility coefficient of oxygen in water. From equations (1) and (2) one obtains:

$$J = -Dk\,\partial p/\partial x \qquad (3)$$

The product Dk in this last equation is known as the permeability coefficient (P) and it is an intrinsic characteristic of the membrane. On the other hand, the partial pressure of the gas must satisfy Fick's second law, i.e.

$$\partial p/\partial t = D\,\partial^2 p/\partial x^2 \qquad (4)$$

where t denotes time. Solution of equation (4) must satisfy the following boundary conditions (see *Figure 2*).

(a) The initial oxygen concentration profile determines $p(x, 0)$.

(b) Once the steady state is reached:

$$p(x=0, \infty) = p_0 \qquad p(x=L, \infty) = p_L \qquad (5)$$

The solution of equation (4) is given by[19]:

$$\frac{p(x,t)-p_0}{p_L-p_0} = \frac{x}{L} + \sum_{n=1}^{\infty} \frac{2}{n\pi}(-1)^n \sin\left(n\pi\frac{x}{L}\right)\exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) \qquad (6)$$

where $\Delta p = p_L - p_0$ is the oxygen partial pressure in the air, since in the electrode this value is zero.

When the diffusion process across the membrane coupled with the electrochemical process in the potentiostatic cell reaches steady-state conditions, the electric current is related to the oxygen flux by:

$$I = -vFAJ \qquad (7)$$

where A is the cathode area, F is Faraday's constant and v the number of electrons transferred in the cathodic reaction. The minus sign comes from the fact that we take the absolute value of I and that, according to the boundary conditions shown in *Figure 2*, we consider $J < 0$. From equations (3) and (6) it follows that:

$$I = vFADk\left(\frac{\partial p}{\partial x}\right)_{x=0} \qquad (8)$$

By substituting equation (6) into equation (8) and further integration of the resulting expression, one obtains that the total electric charge transferred through the membrane in a time t is given by:

$$Q(t) = \int_0^t I(\tau)\,d\tau = vFA\frac{Dk}{L}\Delta p\left(t - \frac{L^2}{6D}\right) \qquad (9)$$

where it was taken into account that:

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n^2}\left[\exp\left(\frac{-n^2\pi^2 Dt}{L^2}\right) - 1\right] = \frac{\pi^2}{12} \qquad (10)$$

and the diffusion coefficient was assumed to be constant. The plot of $Q(t)/vFA$ against t will be a straight line with slope $Dk\Delta p/L$ and the intercept with the time axis in the point $t = L^2/6D$ is known as the time lag. Equations (3) and (9) lead to the expression:

$$I(t\to\infty) = vFA\Delta p(Dk/L) \qquad (11)$$

which suggests that the apparent transmissibility (Dk/L) can be determined from measurements of the steady electric current by means of the relationship:

$$\frac{Dk}{L} = \frac{I(t\to\infty)}{vFA\Delta p} \qquad (12)$$

whereas the apparent permeability is given by:

$$P = Dk = \frac{I(t\to\infty)L}{vFA\Delta p} \qquad (13)$$

Finally, the oxygen diffusion coefficient D was obtained by the time-lag method described before.

RESULTS

In order to study the effect of temperature on the diffusion, the membrane was placed on the electrodes. The vertical hollow cylinder was perfectly adjusted to the membrane and a small quantity ($\approx 0.05\,\text{cm}^3$) of distilled water was introduced by the opening of the cylinder; then the system was deoxygenated in a nitrogen atmosphere until the electric current was reduced to zero as a consequence of the total consumption of oxygen. Nitrogen was no longer pumped into the system and oxygen began to flow into the cavity where the solution is permitted to be in contact with an atmosphere where the oxygen pressure is about 155 mmHg. Oxygen diffused through the membrane of area $(14.25 \pm 0.15) \times 10^{-2}\,\text{cm}^2$ to the other face, situated on the oxygen electrode, where the reduction process takes place.

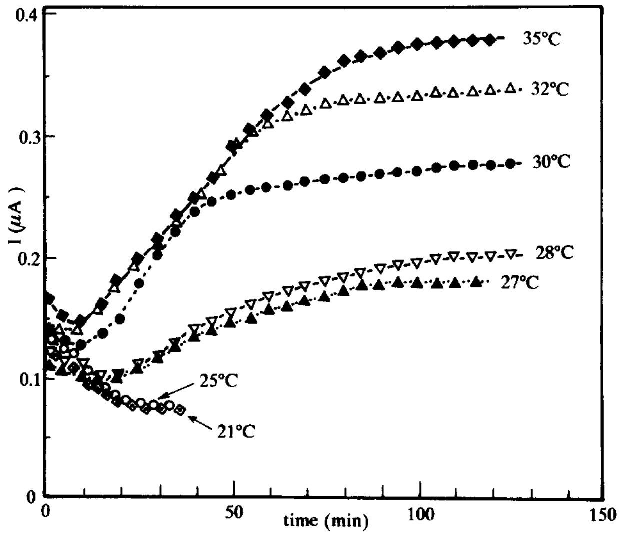

Figure 3 Dependence of the current intensity on time at the temperatures indicated

Table 1 Values of the asymptotic current intensity $I(t\rightarrow\infty)$ and permeability (P) and diffusion coefficients (D) for different temperatures

T (°C)	$I t\rightarrow\infty)$ (μA)	P (barrers)[a]	$10^8\times D$ ($cm^2 s^{-1}$)
21	0.075	0.54	–
25	0.078	0.56	–
27	0.173	1.24	4.47
28	0.200	1.43	5.36
30	0.273	1.97	6.65
32	0.335	2.40	10.50
35	0.377	2.87	11.40

[a] 1 barrer $=10^{-11}$ cm^3 of O_2 (STP) cm/cm^2 s mmHg

Values of the intensity as a function of time, at different temperatures, are given in *Figure 3*. In the vicinity of T_g and at short times, the intensity decreases slightly with time as a consequence of the fact that the small amount of oxygen trapped in the system overcomes the amount of oxygen that diffuses through the membrane. The intensity shows a strong dependence on temperature, and the time necessary to reach steady-state conditions sharply decreases with increasing temperature. By substituting into equation (12) the asymptotic value found for I at each temperature of interest, the results for the permeability coefficient, shown in *Table 1*, are obtained. In the same way, values of the oxygen diffusion coefficient were determined from current–intensity measurements carried out in the steady-state region using the time-lag method described before, that is

$$D=L^2/(6\tau) \tag{14}$$

where τ is the time lag. The results obtained at different temperatures are also shown in *Table 1*.

DISCUSSION

A useful concept in the critical interpretation of diffusive transport processes is fractional free volume[2,20]. Transport of gases through membranes may involve absorption of the penetrant molecules into holes, whose sizes are larger than a critical volume, v^*, followed by jumps to unoccupied sites next to the occupied ones. Diffusion coefficient D is related to the fractional free volume Φ by the following expression[13,14]:

$$D=A\exp(-B'/\Phi) \tag{15}$$

where Φ may be defined as:

$$\Phi=(1-v_0/v) \tag{16}$$

Here v and v_0 represent the specific volume of the membrane at temperatures T and T_0, respectively, the latter being a reference temperature, which can be interpreted as that one at which the free volume would be zero were it not for the formation of the glassy state. By assuming that the free volume is a linear function of temperature, equation (15) becomes:

$$\ln D=A'-m'/(T-T_0) \tag{17}$$

where $m'=B'/\alpha$ and α is the expansion coefficient in the rubbery state.

According to the Cohen and Turnbull theory, the parameter B' is given by[13]:

$$B'=\gamma v^*/v_m \tag{18}$$

where γ is an empirical parameter whose value is close to 1, v^* is the critical volume related, as indicated before, to the size of the permeant molecule and v_m presumably is related to the volume swept by the relaxing segment of the polymer intervening in the formation of holes.

The experimental results were interpreted in terms of equation (17) assuming, as usual, that T_0 is located 50°C below T_g. The results obtained, shown in *Figure 4*, fit fairly well to a straight line with slope $m'=392$ K. At T_g, comparison of equations (15) and (17) leads to:

$$\Phi_g/B'=(T_g-T_0)/m' \tag{19}$$

From these data Φ_g/B' is found to be 0.127. It is worth comparing this value with that found from the analysis of the mechanical and dielectric glass–rubber relaxations of poly(clycohexyl acrylate). These processes are also governed by the free volume, so that their characteristic times can also be expressed in terms of the Doolittle relationship[21] and the Vogel expression[22]:

$$\tau=A'\exp(B/\Phi) \tag{20}$$

$$\ln\tau=A'+m/(T-T_0) \tag{21}$$

where B is given by an expression similar to equation (17), the difference being only that here v^* is the critical volume necessary for a relaxation process to take place. The relaxation times interpreted in terms of equation (20) give straight lines for $T_0=-25$°C (see *Figure 3*)[14]. The slopes of these lines obtained by least-squares analysis have values of 1270 K ($\rho=0.999$) and 1300 K ($\rho=0.9891$) for the dielectric and mechanical relaxations, respectively. From the analysis of both the mechanical and dielectric data, Φ_g/B is found to be 0.038, a result that is significantly larger than the standard value of 0.025 ± 0.005 obtained for most systems[23], presumably as a consequence of the fact that the ratio v^*/v_m for PCA may be lower than for many other polymers. Since the free volume at T_g must be similar for the diffusion and the relaxation processes,

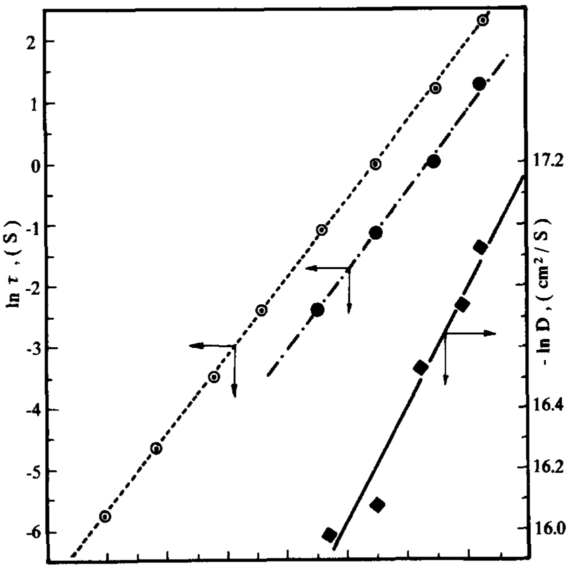

Figure 4 Temperature dependence of the diffusion coefficient (◆), and the relaxation times associated with the dielectric (○) and mechanical (●) glass–rubber absorptions

the differences observed in the ratio should be attributed to the fact that the critical volume necessary for the diffusion to take place is nearly four times lower than the value of this parameter for the mechanical and dielectric processes.

Simulation techniques have been developed that permit one to simulate sampling of static representative conformations of the chains in the glassy state, from which the fractional free volume can be obtained[24]. These methods have been extended to the evaluation of the diffusion coefficient of small molecules through membranes in the rubbery state[3]. The model predicts Arrhenius behaviour for the diffusion coefficient as a consequence of the big changes that take place in the amplitude of the oscillating mode with increasing temperature. It seems that once the penetrant is trapped within a hole, thermal motion of the chains is required to permit its escape.

The diffusion coefficient of oxygen through PCA membranes follows Arrhenius behaviour with an activation energy of 22 kcal mol^{-1}, a surprisingly high value if we consider that the range of activation energies observed in most systems[3] is 1–20 kcal mol^{-1}. Molecular motions inside the chains of poly(cyclohexyl acrylate) involve flipping conformational changes of the cyclohexyl group that give rise to a big mechanical absorption centred at −90°C at 0.1 Hz[14]. Although these conformational transitions together with oscillatory motions occurring in the side groups of PCA chains can aid the diffusion of the gas molecule in the matrix, these effects would only be important for transport in the glassy state. In the rubbery state, diffusion will be mainly conditioned by long-range motions of the main chain. Therefore, the presence of bulky side groups in PCA that hinder the conformational changes in the main chain will not facilitate the transport of gas through the membranes above T_g. In other words, bulky side groups may aid the transport of gas in the glassy state, but probably hinder it in the rubbery state.

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